

TRANSACTIONS
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I—ON A DETERMINATION OF THE FREEZING-POINT DEPRESSION
CONSTANT FOR ELECTROLYTES.—BY THOS. C. HEBB,
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(Communicated on 10th February, 1902, by Prof. J. G. MacGregor.)

In a paper read before the Royal Society of Canada,* Dr. MacGregor has described a method of combining the observations of different observers on the freezing-point depressions of electrolytes, for which the ionization coefficients at 0°C. are known, for the purpose of determining the depression constant for electrolytes. He also applied the method to a few sets of observations made in the Dalhousie College Laboratory, and found that the value so obtained agreed very closely with what one would expect from theory. In a subsequent paper† published by the Nova Scotian Institute of Science, he described a second method, and applied it to all the available data for electrolytes, in which both determinations of the freezing-point depressions, and of the ionization coefficients had been made. At his suggestion, I have applied the first method to the experimental material contained in the second paper, and to a few observations of my own as well, with the result given below.

The method is based upon the assumption, verified by experience, that the formula: $\delta = k(1-a) + la$ —where δ is the

* Trans. Roy. Soc. Can. (2), Vol. 6, Sec. 3, 3, 1900-01.

† Proc. & Trans. N. S. Inst. Sci., Vol. x, p. 211, 1899-00.

equivalent depression, i. e., the depression of the freezing-point divided by the concentration, a is the ionization coefficient at 0°C . and k and l are constants—holds for electrolytes, in which the dilution is sufficient to make the mutual action between the molecules probably negligible. If, in the above formula, the concentration be expressed in gramme-equivalents per litre, the constant k will be the depression of the freezing-point caused by a gramme-equivalent of the undissociated electrolyte, and l will be the depression caused by a gramme-equivalent of the dissociated electrolyte.

Since this holds, it is evident that, if, for any electrolyte, we plot equivalent depressions δ against ionization coefficients a , we will at sufficient dilution get a straight line. Hence, knowing the equivalent depressions, and the ionization coefficients for different concentrations, for any electrolyte, we can draw in the ionization-equivalent depression curve. Then, finding that portion of the curve, which seems to be rectilinear, we can draw in the straight line, which best represents the results. The equation of this line from the above is $\delta = k(1-a) + la$; and we may determine k and l by taking two points on the line, substituting the values of δ and a so obtained in the equation, and then solving the two simultaneous equations obtained.

Now it is clear that the constants, k and l , bear a simple relation to the depression constants, i. e., to the depression of the freezing-point produced by a gramme-molecule of the undissociated electrolyte, and the depression produced by a gramme-ion of the free ions. Call these two constants m and i .

In the case of NaCl , KCl , HCl , NH_4Cl , KNO_3 , HNO_3 and KOH , since each gramme-equivalent is a gramme-molecule, we have $k = m$; also, since each molecule breaks up into two ions each of which is equally effective in lowering the freezing-point, we have $l = 2i$.

In the case of BaCl_2 , K_2SO_4 , Na_2SO_4 and H_2SO_4 , since each gramme-molecule contains two gramme-equivalents, we have $k = \frac{1}{2}m$; and we have $l = \frac{3}{2}i$, if we assume the molecule in

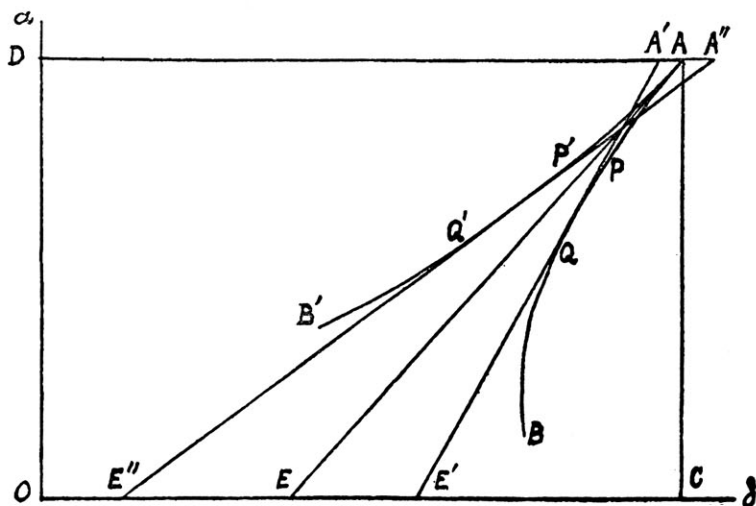
each case to break up into three ions, as, according to Prof. MacGregor's Diagram of Freezing-point depressions, it seems to do.

In the case of MgSO_4 each gramme-molecule contains two gramme-equivalents, hence $k = \frac{1}{2}m$; and since each molecule breaks up into two ions we get $l = i$.

In the case of H_3PO_4 , if each gramme-molecule contains three gramme-equivalents, we have $k = \frac{1}{3}m$; also, if each molecule breaks up into two ions, as Loomis's and Jones's results seem to imply, we have $l = \frac{2}{3}i$.

As the constants, m and i , depend so simply on the constants, k and l , the accuracy of their determination will depend on the accuracy with which we can determine k and l . Dr. MacGregor has shewn that the values of l can be determined with a much greater degree of accuracy than can k .

Thus if AB or AB' be the true curve representing the relation between δ and a —the curves for different electrolytes bend in different ways—then the equation $\delta = k(1-a) + la$ will represent the straight line AE , *i. e.*, the tangent to the curve at infinite dilution if AC represents unity.



If in this equation $a=1$ then $\delta=l$ which is represented on the diagram by DA. Again if $a=0$ then $\delta=k$ which is represented by OE on the diagram. Now suppose that in drawing in our straight line we consider some portion as QP or Q'P' as straight, and hence get the line as represented by our formula to be A''E'' or A'E'. In this case our l will be A''D or A'D instead of the true value AD, and k will be OE' or OE'' instead of OE. The error in l is A''A or A'A, while that in k is EE'' or EE'. It is plain that AA'' or AA' is less than EE'' or EE', *i. e.*, that the accuracy with which l is determined is greater than that with which k is determined. Hence the values of i are affected with a smaller error than are those of m .

Since the depressions for dilute solutions are affected with a considerable error, the part of the ionization-equivalent depression curve near A is very untrustworthy. This is shewn by Dr. MacGregor in one of the papers referred to above. He has pointed out that the curves of the different observers for the same electrolyte deviate at great dilution, some to the right and others to the left of what their general course is at moderate dilution. Not only this, but the different observations of the same observer become very irregular as dilution increases.

As, therefore, the curves of the different observers have this rightward or leftward tendency—and sometimes to a great extent—as dilution increases, it is evident that we get better values of k and l , if we obtain them from a part of the ionization-equivalent depression curve, which corresponds to a concentration at which trustworthy determinations of the depressions can be made, than if we use the very erratic observations at high dilution. I have, therefore, in the determinations of k and l used only the observations on solutions of moderate dilution. As, however, some curves begin to curve rapidly as the concentration increases, even at an early stage, one has to use some discretion in choosing a part of the curve, which is least affected on the one hand by the natural bend of the curve, and on the other by the bend due to the error of method of the observer.

The data, as I have indicated, are taken from the second of the papers referred to above. Before, however, plotting the ionization-equivalent depression curve, I plotted in each case the equivalent depression against concentration, and drew in the smooth curve which best represented the results, so that approximately as many points fell on one side of the curve as on the other. In drawing in this curve, however, I did not use many of the observations—only those of the stronger concentrations. This was done in order to get rid, as much as possible, of the error due to the rightward or leftward tendency of the observations; for, had I plotted all the points and then drawn in the smooth curve which best represented them, these latter erratic points would have given a rightward or leftward tendency even to the part of the curve corresponding to the stronger concentrations. Hence, as a general thing, I discarded all but three or four of the observations on the stronger concentrations. In cases where I have kept more it is due to one of three things: (1) because the points were close together; (2) because there was very little rightward or leftward tendency to the ionization-equivalent depression curve, or (3) because the ionization-equivalent depression curve for these stronger concentrations had a rapid natural bend to it. The information in (2) and (3) was ascertained by a preliminary plotting of ionization coefficients against equivalent depressions. Having thus drawn in the smooth concentration-equivalent depression curve, I read off the values of the equivalent depressions corresponding to the given concentrations, and have given them in brackets alongside of the observations themselves.

I then plotted these corrected equivalent depressions against their corresponding ionization coefficients, and finding by inspection the portion of the curve thus obtained, which was straight, I drew in the straight line which I thought best represented the results. In drawing in this straight line I generally gave more weight to points corresponding to solutions of greater concentration. This straight line was then treated as pointed out above, and k and l were thus obtained.

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The following table gives all the data together with the values of k and l thus obtained. The values of the ionization coefficients given were taken directly from the second of Dr. MacGregor's papers referred to above. The letters i and e which follow the coefficients indicate as to whether the values were obtained by interpolation or extrapolation. While the letters A, B, D and W refer to the observers Archibald, Barnes, Déguisne and Whetham.

TABLE I.

Concentration. (gr eq./l.)	Ionization Coefficients at 0° C.	Equivalent Depression.	Concentration. (gr. eq./l.)	Ionization Coefficients at 0° C.	Equivalent Depression.
KCl. (Loomis.) <i>k</i> =2.065; <i>l</i> =3.673.			KCl. (Ponsot.) <i>k</i> =1.920; <i>l</i> =3.687.)		
.01	.943 i. B.	3.60	.1468	.846 i. B.	3.413 (3.415)
.02	.923 “	3.55	.1688	.840 “	3.406 (3.404)
.03	.910 “	3.52 (3.528)	.2344	.827 “	3.392 (3.381)
.035	.905 “	3.53 (3.519)	.2456	.825 “	3.375 (3.378)
.05	.892 “	3.50 (3.498)	.2472	.825 “	3.378
.1	.862 “	3.445 (3.450)	.2544	.824 “	3.377
.2	.832 “	3.404			
.4	.804 “	3.353			
KCl. (Jones.) <i>k</i> =2.180; <i>l</i> =3.678.			KCl. (Wildermann.) <i>k</i> =2.034; <i>l</i> =3.639.		
.04	.900 i. B.	3.5325	.03883	.900 i. B.	3.515 (3.5235)
.0592	.885 “	3.5067	.03884	.900 “	3.532 (3.5235)
.078	.873 “	3.4923 (3.487)	.07652	.873 “	3.491 (3.489)
.09646	.863 “	3.4688 (3.473)	.07668	.873 “	3.487 (3.489)
.2	.832 “	3.4300			
.23	.821 “	3.4107			
KCl. (Raoult.) <i>k</i> =1.846; <i>l</i> =3.652.			KCl. (Hebb.) <i>k</i> =1.755; <i>l</i> =3.695.		
.05825	.904e. W.	3.478	.0628	.882 i. B.	3.451 (3.465)
.1168	.878 “	3.431	.1065	.859 “	3.415 (3.430)
			.2121	.830 “	3.404 (3.375)
			.3186	.817 “	3.340
KCl. (Abegg.) <i>k</i> =1.344; <i>l</i> =3.719.			NaCl. (Loomis.) <i>k</i> =2.140; <i>l</i> =3.722.		
.0469	.895 i. B.	3.47	.08	.860 i. B.	3.501
.0583	.887 “	3.45	.09	.855 “	3.494 (3.493)
.0697	.878 “	3.43	.10	.850 “	3.484 (3.485)
			.20	.815 “	3.439

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TABLE I.—Continued.

Concentration. (gr. eq./l.)	Ionization Coefficients at 0° C.	Equivalent Depression.	Concentration. (gr. eq./l.)	Ionization Coefficients at 0° C.	Equivalent Depression.
NaCl. (Jones.) $k=2.050$; $l=3.726$.			HCl. (Loomis.) $k=2.095$; $l=3.643$.		
.0790	.861 i. B.	3.492	.01	.982 i. B.	3.61 (3.615)
.0882	.856 "	3.483 (3.484)	.02	.972 "	3.60 (3.599)
.0973	.851 "	3.477 (3.476)	.05	.955 "	3.59 (3.574)
.1063	.848 "	3.469	.1	.933 "	3.546 (3.555)
.15	.831 "	3.447 (3.442)	.2	.910 "	3.565
.1925	.818 "	3.418 (3.424)	.3	.897 "	3.612
.2329	.805 "	3.414	HCl. (Jones.) $k=1.950$; $l=3.684$.		
NaCl. (Abegg.) $k=.800$; $l=3.957$.			.08127	.940 i. B.	3.5856 (3.580)
.0439	.882 i. B.	3.57 (3.580)	.1025	.933 "	3.5609 (3.568)
.0653	.867 "	3.55 (3.537)	.1228	.928 "	3.5692 (3.565)
.0871	.856 "	3.50	NH ₄ Cl. (Loomis.) $k=1.380$; $l=3.700$.		
.1083	.847 "	3.47	.01	.951 i. D.	3.56 (3.585)
NaCl. (Arrhenius.) $k=1.992$; $l=3.697$.			.02	.931 "	3.56 (3.540)
.194	.816 i. B.	3.54	.035	.914 "	3.50
.324	.781 "	3.51	.05	.900 "	3.48
NaCl. (Ponsot) $k=2.000$; $l=3.728$.			NH ₄ Cl. (Jones.) $k=2.050$; $l=3.692$.		
.1318	.836 i. B.	3.445	00997	.951 i. D.	3.6108
.1808	.821 "	3.418 (3.419)	.0595	.892 e. D.	3.5143
.2016	.814 "	3.413 (3.411)	KNO ₃ . (Loomis.) $k=1.580$; $l=3.682$.		
.2248	.808 "	3.403 (3.405)	.025	.899 i. D.	3.46
.2288	.806 "	3.405 (3.404)	.05	.876 "	3.41
			.1	.832 e. D.	3.314
			.2	.789 "	3.194

TABLE I.—Continued.

Concentration. (gr. eq. /l.)	Ionization Coefficients at 0° C.	Equivalent Depression.	Concentration. (gr. eq. /l.)	Ionization Coefficients at 0° C.	Equivalent Depression.
K ₂ S O ₄ . (Ponsot.) <i>k</i> =.874; <i>l</i> =2.834.			H ₂ S O ₄ . (Ponsot.) <i>k</i> =.617; <i>l</i> =2.797.		
.0724	.731 i. A.	2.307	.2570	.587 i. B.	1.895 (1.897)
.0752	.726 "	2.301	.2580	.587 "	1.899 (1.897)
.2295	.635 "	2.113 (2.115)	.4476	.565 "	1.850
.2360	.633 "	2.110 (2.109)	.4516	.565 "	1.849
.4140	.596 "	2.012 (2.010)	H ₂ S O ₄ . (Wildermann.) <i>k</i> =1.080; <i>l</i> =2.565.		
.4280	.594 "	2.002 (2.005)	.1358	.622 i. B.	2.004
Na ₂ S O ₄ . (Loomis.) <i>k</i> =1.100; <i>l</i> =2.815.			.1930	.599 "	1.970
.20	.624 i. A.	2.170	Mg S O ₄ . (Loomis.) <i>k</i> =.713; <i>l</i> =1.793.		
.40	.546 "	2.036	.04	.522 i. D.	1.277
.60	.511 "	1.938	.06	.485 "	1.237
Na ₂ S O ₄ . (Arrhenius.) <i>k</i> =1.180; <i>l</i> =2.950.			Mg S O ₄ . (Jones.) <i>k</i> =1.074; <i>l</i> =1.849.		
.234	.607 i. A.	2.205	.015972	.614 i. D.	1.5590
.390	.549 "	2.095	.017940	.608 "	1.5496 (1.545)
H ₂ S O ₄ . (Loomis.) <i>k</i> =.731; <i>l</i> =2.826.			.019904	.596 "	1.5323 (1.535)
.20	.598 i. B.	1.984	.03950	.521 "	1.4912 (1.486)
.40	.570 "	1.925	.05872	.502 "	1.4391 (1.444)
H ₂ S O ₄ . (Jones.) <i>k</i> =.792; <i>l</i> =2.767.			H ₃ P O ₄ . (Loomis.) <i>k</i> =.654; <i>l</i> =1.1198.		
.11358	.633 i. B.	2.0514 (2.042)	.03	.614 i. D.	0.94
.15472	.612 "	1.9952 (2.001)	.06	.513 "	0.893
.19450	.598 "	1.9732	H ₃ P O ₄ . (Jones.) <i>k</i> =.620; <i>l</i> =1.338.		
.2330	.586 "	1.9498	.019605	.669 i. D.	1.0967 (1.101)
			.027705	.627 "	1.0721 (1.069)
			.03279	.602 "	1.0522

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TABLE I.—Continued.

Concentration (gr. eq. /l.)	Ionization Coefficients at 0° C.	Equivalent Depression.	Concentration (gr. eq. /l.)	Ionization Coefficients at 0° C.	Equivalent Depression.
K O H. (Loomis.) $k=2.256$; $l=3.516$			Ba Cl ₂ . (Ponsot.) $k=1.136$; $l=2.786$.		
.05	.943 e. D.	3.44	.05520	.796 e. W.	2.446
.10	.932 "	3.43	.0620	.790 "	2.436
H N O ₃ . (Jones.) $k=2.640$; $l=3.765$.			.0680	.785 "	2.426 (2.427)
.03119	.958 e. D.	3.7179	.0774	.771 "	2.416 (2.415)
.05103	.949 "	3.7076	.2060	.717 "	2.316
K O H. (Jones) $k=2.019$; $l=3.699$.			.2095	.716 "	2.320 (2.315)
.01069	.964 e. D.	3.6296 (3.640)	.2235	.710 "	2.309 (2.311)
.03163	.950 "	3.6263 (3.616)	.3100	.685 "	2.297
.05174	.942 "	3.5756 (3.600)	K ₂ S O ₄ . (Loomis.) $k=1.118$; $l=2.752$.		
.07481	.935 "	3.6142 (3.590)	.02	.821 i. A.	2.46
Ba Cl ₂ . (Loomis.) $k=1.198$; $l=2.743$.			.04	.772 "	2.38
.02	.860 i. W.	2.495 (2.505)	.1	.705 "	2.271
.04	.820 e. W.	2.475 (2.465)	.2	.645 "	2.1585
.1	.768 "	2.385	.4	.598 "	2.0335
.2	.724 "	2.345	.6	.583 "	1.9455
.4	.658 "	2.3275	K ₂ S O ₄ . (Jones) $k=.849$; $l=2.879$.		
Ba Cl ₂ . (Jones) $k=1.414$; $l=2.731$.			.1357	.677 i. A.	2.231 (2.234)
.011964	.889 i. W.	2.5823 (2.590)	.152	.668 "	2.208 (2.210)
.01394	.880 "	2.5753	.16765	.661 "	2.197 (2.192)
.01592	.872 "	2.5754 (2.565)	.1826	.654 "	2.178 (2.176)
.01788	.866 "	2.5560	.19685	.647 "	2.160 (2.162)
.02	.860 "	2.550	K ₂ S O ₄ . (Abegg.) $k= .931$; $l=2.771$.		
Ba Cl ₂ . (Jones) $k=1.414$; $l=2.731$.			.01734	.829 i. A.	2.47
.011964	.889 i. W.	2.5823 (2.590)	.0216	.815 "	2.43 (2.428)
.01394	.880 "	2.5753	.0258	.803 "	2.40 (2.402)
.01592	.872 "	2.5754 (2.565)	.0299	.794 "	2.385
.01788	.866 "	2.5560	Ba Cl ₂ . (Jones) $k=1.414$; $l=2.731$.		
.02	.860 "	2.550	K ₂ S O ₄ . (Abegg.) $k= .931$; $l=2.771$.		

The following table gives the values of the constants k and l given in table I. together with the values of m and i —*i. e.*, the depressions of the freezing-point due to a gramme-molecule of the undissociated salt, and that due to a gramme-ion of the dissociated salt—as obtained from them.

TABLE II.

Electro-lyte.	Observer.	Ionization Constants.		Depression Constants for	
		k	l	Undissociated Molecules (m).	Free Ions (i).
KCl	Loomis	2.065	3.673	2.065	1.837
"	Jones	2.180	3.678	2.180	1.839
"	Raoult	1.846	3.652	1.846	1.826
"	Abegg	1.344	3.719	1.344	1.860
"	Wildermaun.	2.034	3.689	2.034	1.845
"	Ponsot	1.920	3.687	1.920	1.844
"	Hebb	1.755	3.695	1.755	1.848
NaCl	Loomis	2.140	3.722	2.140	1.861
"	Jones	2.050	3.726	2.050	1.863
"	Abegg	.800	3.957	.800	1.979
"	Arrhenius	1.992	3.697	1.992	1.849
"	Ponsot	2.000	3.728	2.000	1.864
HCl	Loomis	2.095	3.643	2.095	1.822
"	Jones	1.950	3.684	1.950	1.842
NH ₄ Cl	Loomis	1.380	3.700	1.380	1.850
"	Jones	2.050	3.692	2.050	1.846
KNO ₃	Loomis	1.580	3.682	1.580	1.841
HNO ₃	Jones	2.640	3.765	2.640	1.883
KOH	Loomis	2.256	3.516	2.256	1.758
"	Jones	2.019	3.699	2.019	1.850
BaCl ₂	Loomis	1.198	2.743	2.396	1.829
"	Jones	1.414	2.734	2.828	1.823
"	Ponsot	1.136	2.786	2.272	1.857
K ₂ SO ₄	Loomis	1.118	2.752	2.236	1.835
"	Jones	.849	2.879	1.698	1.919
"	Abegg	.901	2.771	1.802	1.847
"	Ponsot	.874	2.834	1.748	1.889
Na ₂ SO ₄	Arrhenius	1.180	2.950	2.360	1.967
"	Loomis	1.100	2.815	2.200	1.877
H ₂ SO ₄	Loomis	.731	2.826	1.462	1.884
"	Jones	.792	2.767	1.584	1.845
"	Ponsot	.617	2.797	1.234	1.865
"	Wildermann.	1.080	2.565	2.160	1.710
MgSO ₄	Loomis	.713	1.793	1.426	1.793
"	Jones	1.074	1.849	2.148	1.849
H ₃ PO ₄	Loomis	.654	1.120	1.962	1.680
"	Jones	.620	1.338	1.860	2.007

One sees from an inspection of this table that the values of i , though they vary considerably, are in most cases not far from

the value expected from theory. In the case of the undissociated molecules, however, the variation of their values is much greater. As the depression produced by molecules is supposed on theoretical grounds to be the same as that produced by free ions, the difference between the variations of m and i is probably due to the different degrees of accuracy with which, as seen above, m and i are capable of determination.

If we assume, as is customary, that the depression produced by the molecules, whether they are undissociated molecules or free ions, is the same for all electrolytes in dilute solution, we can arrive at better values of both m and i by finding the mean values. This becomes obvious when we take into consideration the sources of error which affect the values of k and l . For the straight line, from which k and l are determined, may be either too high or too low; or it may be too much or too little inclined to the equivalent depression axis. The line may be too high or too low because of defective observations of depression, defective values of ionization coefficients, or the way in which I have drawn it in. So far, at least, as two of these sources of error are concerned, the resulting errors will in some cases be positive and in others negative; and in finding the average these errors will in part cancel one another. Defective inclination of the line may be due, in addition, to the characteristic error of the observer's method, which may be such as to make the curve at great dilution go off either to the right or the left as dilution increases, or to the natural bend of the curve itself which may be either to the right or left as concentration increases. The errors due to these sources will also be, in some cases, positive, and in others negative, and hence will practically neutralize one another on averaging.

The determinations of the above table are not all of the same order of trustworthiness. Some are based on freezing-point observations made by means of old methods; others on those of newer and more accurate methods. Some are based on many observations, others on few; some on observations in good agreement, others on more erratic series. In some cases, also, the ionization coefficients employed are more trustworthy than in

others If an estimate could be made of the relative value of the various determinations, the weighted mean would give a closer approximation to the true values of the depression constants, than can be given by a mere average. I have not attempted, however, to attach weights to the determinations, being unable to do so with any confidence.

Assuming that averaging will eliminate the greater part of the errors we get as the values of m and i , 1.932 and 1.851 respectively. The value for i is undoubtedly the more accurate of the two; and, as we assume that undissociated molecules have the same effect as free ions, the value of m is to be taken as 1.851 also. That the average value of m is so much greater than that of i may be due not only to the defects of the method employed in determining it, but to the fact that the bend of the curve of an electrolyte is more likely to be to the right than to the left, as concentration increases. For it is only where association of molecules takes place that it bends to the left.

Some of the sets of observations given in the paper, from which I have taken my data, I did not use. A few of these sets were so erratic that I could make nothing out of them. The other cases, however, had been worked out by Dr. MacGregor, and, hence, I did not think it worth my while to do so. If, now, I combine my results with those obtained by him, I will, with the exception of the few sets mentioned above, have made use of all available data. The mean values of m and i , as given by him, are 1.895 and 1.850 respectively and hence the values of m and i as given by averaging his mean values with mine are 1.913 and 1.851.

The above result is in agreement with that reached by Prof. MacGregor by means of the second method referred to above. The conclusion he arrived at was that, for all the electrolytes examined, the curves of his diagram were consistent with the depression constant having a common value of about 1.85. That the two methods should give results which are not only in close agreement with one another, but are also in close agreement with the value of the depression constant given by Van 't Hoff's theoretical expression for it, must be regarded as of considerable interest.